Report No. FHWA-KS-99-5
Interim Report

RAPID AND SIMPLE METHOD FOR BINDER OXIDATIVE AGING

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August 1999

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1. Report No. KS-99-5	**2. Government Accession No.**	**3. Recipient Catalog No.**
4 Title and Subtitle RAPID AND SIMPLE METHOD FOR BINDER OXIDATIVE AGING		**5 Report Date** August 1999 **6 Performing Organization Code**
7. Author(s) S.W. Bishara, R.E. Robertson, R.L. McReynolds, Donna Mahoney		**8 Performing Organization Report No. 282** FHWA-KS-99-5
9 Performing Organization Name and Address Kansas Department of Transportation Docking State Office Bldg. Topeka, Kansas 66612		**10 Work Unit No. (TRAIS)** **11 Contract or Grant No.** SPR 73-1
12 Sponsoring Agency Name and Address Federal Highway Administration 3300 SW Topeka Blvd., Suite 1 Topeka, Kansas 66611		**13 Type of Report and Period Covered** Final Report July 1998 to August 1999 **14 Sponsoring Agency Code**
15 Supplementary Notes		

16 Abstract

A rapid and simple method for simulating binder aging is presented. Using the eight SHRP core asphalts, treating neat asphalt with microwave radiation for 7 hr and 20 min at 143°C and 440 psi yields a residue equivalent to that of “RTFOT + PAV.” To test ability of microwave energy (dielectric heating) to simulate “RTFOT + PAV” aging (conductive heating), six different tests were used to compare physical, chemical, and physicochemical changes resulting from the two modes of aging. The six tests are: intermediate – temperature stiffness, low-temperative stiffness, asphaltene content, high-performance size exclusion chromatography (HPSEC), asphalt relative total polarity, and infrared spectroscopy.

Conductive heating (PAV, with or without RTFOT) under the conditions of microwave treatment (7 hr and 20 min at 143°C and 300 psi – for safety, 440 psi could not be used with PAV) yields a residue that shows clumping in the pan, and nonhomogeneity that prevented rheological testing. Therefore, conductive heating cannot replace dielectric heating for rapid aging. Alternatively, applying dielectric heating at the Superpave conditions of 20 hr at 100°C and 300 psi, gives rheological changes equivalent to those produced by both the RTFOT plus the 20 hr of PAC at similar conditions. Thus, dielectric heating enhances oxidation even at 100°C. The enhancement is more pronounced at higher temperatures (143°C) with a 70 percent saving of time.

17 Key Words Short-term aging, Long-term aging, Microwave	**18 Distribution Statement** No restrictions. This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161 .

19 Security Classification (of this report) Unclassified	**20 Security Classification (of this page)** Unclassified	**21 No. of pages** 35	**22 Price**

Form DOT F 1700.7 (8-72)

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACKNOWLEDGENT

The authors would like to thank the FHWA and its Kansas Division for their cooperation to accomplish this work. Thanks are due to Dr. H. Bahia, Dr. E. Bastian, Dr. B. Chollar, Dr. David Jones, Dr. Gayle King, and Mr. M. Zupanick for their valuable discussions and suggestions. We also would like to thank Western Research Institute for the IR spectra.

ABSTRACT

A rapid and simple method for simulating binder aging is presented. Using the eight SHRP core asphalts, treating neat asphalt with microwave radiation for 7 hr and 20 min at 143°C and 440 psi yields a residue equivalent to that of Rolling Thin Film Oven Test plus Pressure Aging Vessel ("RTFOT + PAV"). To test ability of microwave energy (dielectric heating) to simulate "RTFOT + PAV" aging (conductive heating), six different tests were used to compare physical, chemical, and physicochemical changes resulting from the two modes of aging. The six tests are: intermediate – temperature stiffness, low – temperature stiffness, asphaltene content, high – performance size exclusion chromatography (HPSEC), asphalt relative total polarity, and infrared spectroscopy.

Conductive heating (PAV, with or without RTFOT) under the conditions of microwave treatment (7 hr and 20 min at 143°C and 300 psi – for safety, 440 psi could not be used with PAV) yields a residue that shows clumping in the pan, and nonhomogeneity that prevented rheological testing. Therefore, conductive heating cannot replace dielectric heating for rapid aging. Alternatively, applying dielectric heating at the Superpave conditions of 20 hr at 100°C and 300 psi, gives rheological changes equivalent to those produced by both the RTFOT plus the 20 hr of PAV at similar conditions. Thus, dielectric heating enhances oxidation even at 100°C. The enhancement is more pronounced at higher temperatures (143°C) with a 70 percent saving of time.

KEY WORDS: Short-term aging; Long-term aging; Microwave

INTRODUCTION

Our previous work (1, 2) has shown the potential of using microwave radiation to simulate oxidative aging of asphalt. Due to unavailability then of a scientific microwave unit, a household microwave oven was used. Two major concerns were raised. First, there was no means for continuously monitoring the sample temperature during microwave treatment. Second, the uncovered Petri dishes used as sample containers allow escape of some volatile constituents over the course of treatment and do not permit pressurizing the asphalt material.

The last 10 years have seen an ever-increasing use of microwave radiation (dielectric heating, in-situ heating) especially in organic synthetic research, the undergraduate laboratory, and industrial production. Several books (3-5) and reviews (6-10) describe theoretical and practical aspects of the subject. Over 250 papers have been published since 1986 to document the dielectric heating enhancement of reaction kinetics for a wide variety of organic reactions, e.g., oxidation. Recently (11), the selective rate of dielectric heating was used to rapidly determine asphalt total polarity (12), as well as sulfur and sulfide content of the eight SHRP core asphalts.

The increased application of microwave energy ushered in technological improvements. Scientific microwave instruments (11) are now available to allow continuous monitoring of temperature and pressure. These controls are essential for laboratory aging of binders. The fluorooptic temperature probe is a quartz optical fibre with its tip covered with manganese-activated magnesium fluorogermanate. Sample containers that can tolerate up to 600 psi are commonly used. The typical scientific microwave instrument consists of five major components: a microwave generator (magnetron), wave guide, microwave cavity, mode stirrer, and turntable (3, 11).

Laboratory aging of asphalt is central to the performance graded (PG) system. Approximately half the number of tests and two-thirds of the testing time deal with measurements performed on the PAV residue. To get the PAV residue, the binder is first subjected to short-term aging (TFOT or RTFOT). That is, a total of about 24 hr, or more, is required to obtain the PAV residue. It may not be surprising that simulation of oxidative aging has been reported a bottleneck in the PG system (13). An aging technique that simulates oxidative aging in a shorter time period is in demand.

The present work describes a microwave treatment procedure that simulates the short- plus long-term aging, in one step, in slightly more than 7 hr, that is, treating neat asphalt for this time period yields the PAV-residue equivalent.

EXPERIMENTAL

Apparatus and Materials

A scientific microwave unit, model MDS 2100, from CEM Corporation was used. This is the same unit used previously (11). Upon our request, the instrument now has 1250-W output power. The unit has a built-in fluorooptic temperature probe. A polypropylene turntable can hold up to six heavy duty vessels (HDV). The unit is furnished with an alternating turntable drive system. During treatment, the turntable rotates 360 degrees, then reverses direction to prevent the pressure tubings and fluorooptic temperature probe from being entangled and damaged.

Each HDV has a liner made of TFM® polytetrafluoroethylene, that is about 3.0 cm in diameter and 13.0 cm high. The liner is surrounded by an advanced composite sleeve that rests on an Ultem® polyetherimide heat shield. The liner, sleeve, and heat shield are inside a polypropylene body that is covered by a threaded polypropylene cap. At the cap center there is a Teflon® polyfluoroalkoxy ethylene cover that screws in at the top to a control fitting with three openings. One opening holds a rupture membrane and acts as a ventilation port for safety. The second is the temperature control port through which passes a pyrex thermowell to protect the fluorooptic temperature probe from contamination, but still provides contact with the sample material for sensing its temperature. Because there is only one temperature probe, only one of the vessels has a temperature port with a thermowell; the other vessels have a closed nut instead. The third opening is the pressure port and allows connection of the vessel, via teflon tubing, to an air cylinder with a pressure gauge for pressure control. The teflon tubing passes from the vessel to the air cylinder through 1 of 4 inlet/outlet ports existing on the side of the microwave cavity (3, 11).

A printer generates a hard copy of the data and a graph showing the change of temperature every 30 sec. of treatment time.

The eight SHRP core asphalts were used.

Procedure

Daily calibration was carried out to correlate the power percent setting of the microwave unit with the corresponding output power in watts. Calibration is done by recording the temperature of 1000 g of water (practically 1L) before and after heating in the microwave unit for 120 sec. The power, P, absorbed by water in watts ($Joule.s^{-1}$) is calculated from the equation:

$$P = \frac{(K)\,(C_p)\,(m)\,(\Delta T),}{t} \qquad W \tag{1}$$

where K = conversion factor for thermochemical $cal.s^{-1}$ to watts and equals 4.184; C_p = specific heat of water in $cal.g^{-1}.\ {}^{\circ}C^{-1}$ and equals 0.9997 at 25°C; m = mass of water sample in g; ΔT =

change in temperature, °C, due to absorption; and t = time in sec. Substituting in equation (1) we get:

$$P = 34.86\,(\Delta T) \qquad W \tag{2}$$

The calibration is carried out at three power settings of 90, 80, and 70 percent. Plotting output power (W) vs. power setting gives a straight line that connects the three points.

Based on the number of sample vessels used, two procedures have been developed.

<u>Procedure A</u> Heat the neat asphalt in a convection oven for ½ hr at 150°C. Weigh each of two liners to the nearest 0.01 g. Pour 11.0 ± 0.1 g in each liner. Assemble each vessel and tighten the caps. Place the two vessels, opposite to each other, on the turntable. Connect the vessels to a compressed air cylinder via polyethylene tubings that pass through the inlet/outlet ports. Insert the temperature probe in one of the vessels. Use microwave radiation to warm the vessels from room temperature to 27°C using a separate program (5 min ramp and a maximum temperature of 27°C). Abort when sample temperature reaches 27°C. This brings the samples to a common start. Program the microwave unit to run the aging process as follows:

Stage I: 60 min, using 930 ± 10 W output power; temperature increased regularly from 27°C to 143°C (ramp).

Stages II to VI: 60 min each, using 1035 ± 10 W output power; temperature maintained at 143°C.

Stages VII and VIII: 50 and 30 min, respectively, using 1035 ± 10 W output power; temperature maintained at 143°C.

Stages I to VII: 20 percent fan speed; **Stage VIII**: 40 percent fan speed.

All stages apply 3.08 MPa (440 psi) air pressure.

After microwave treatment, use pressure relief valve to release air pressure over 4 – 5 min. Detach and remove the vessels from the unit. Place the vessels in a convection oven for 5 min at 150°C. Pour in storage can, and degas.

Procedure B Similar to procedure A, except that six vessels were used per run.

RESULTS AND DISCUSSION

Microwave Aging vs. "RTFOT + PAV" Aging

In order to verify ability of microwave energy to simulate oxidative aging akin to "RTFOT + PAV" aging, six tests corresponding to six techniques were performed to compare the physical, chemical, and physicochemical properties of the residues obtained from the two methods of aging. Procedure A was used for the six tests. It was possible to collect ca. 20 g per run. Procedure B was later developed to allow collecting of a larger sample size.

1. Intermediate-temperature stiffness: This was measured according to AASHTO TP5 at KDOT then at the Asphalt Institute (AI). Two separate runs of each asphalt were microwave treated and tested on DSR at KDOT (Table 1), then mixed before sending to AI for further testing [this provides enough material for AI to test for intermediate-temperature stiffness (Tables 1, 2) and low- temperature stiffness (Tables 4, 5)]. Table 1 shows that all of the eight core asphalts, except AAD-1, fall in the same grade regardless of the aging method. Asphalt AAD-1 is switched from the 19°C grade using "RTFOT + PAV" to 16°C grade using microwave radiation. But the difference in $G^*.\sin\delta$ between the two aging methods, calculated as percentage of their mean, is 14.2 percent at 19°C using AI data, and less than that using KDOT data. According to ASTM C670 and AASHTO TP5, the acceptable difference between any two results, for the same method by a single operator, calculated as percentage of their mean should not exceed the coefficient of variation (C.V.) times 2.83, that is, 7.9 x 2.83 or 22.4

percent. Therefore, for AAD-1 the difference in G*.sinδ between the two aging methods (14.2 percent) falls within the expected normal distribution of data for the same method (14).

Table 2 compares the critical temperature (temperature at which binder meets specification limit) after microwave aging with the critical temperature after "RTFOT + PAV" aging. The difference, ΔT, did not exceed 2.6°C, and the ΔT_{ave} equals 1.2°C.

To test repeatability of the microwave aging method, six replicates of asphalt AAD-1 were treated according to procedure A. Table 3 shows that the percent variation for KDOT and AI data was 26.5 and 6.9 percent, respectively. To calculate the acceptable range (d2s, percent), the C.V. (7.9) is multiplied by a factor of 4.0 (for six measurements, see ASTM C670), that is, 31.6 percent. Therefore, the percent variation for G*.sinδ falls well within the acceptable range of variation according to AASHTO TP5.

2. <u>Low-temperature stiffness and slope:</u> This was measured according to AASHTO TP1 at the AI. Table 4 shows that all of the eight core asphalts, except AAK-1, fall in the same grade regardless of the aging method. Asphalt AAK-1 moved one grade. However, at –12°C the difference in stiffness, S, between the two aging methods, measured as percentage of their mean, is (154 – 139) x 100 / 147 or 10.2 percent; for m, the difference is (0.391 – 0.372) x 100 / 0.382 or 5.0 percent. The 1s, percent limit reported in AASHTO TP1 (according to ASTM C670), sets the acceptable limit of difference between any two results obtained by a single operator using the same method, and measured as percentage of their mean, to equal C.V. times 2.83, that is, 3.2 x 2.83 or 9.1 percent for S, and 1.4 x 2.83 or 4.0 percent for m. The differences of 10.2 percent for S and 5.0 percent for m compare reasonably well with the TP1 acceptable limits of 9.1 and 4.0 percent, respectively.

Table 5 compares T_C, °C obtained after microwave aging with that obtained after "RTFOT + PAV" aging. The difference, ΔT, did not exceed 2°C, and the ΔT_{ave} was 0.9°C.

Repeatability of low-temperature rheological measurements after microwave aging was determined by running six replicates of asphalt AAD-1 according to procedure A. Table 6 shows that the percent variation was 10.1 and 6.5 percent for S and m, respectively. According to AASHTO TP1, the C.V. is 3.2 and 1.4 for S and m, respectively. For the six replicates, the acceptable range is 3.2 x 4.0 or 12.8 and 1.4 x 4.0 or 5.6 for S and m, respectively (see ASTM C670). Therefore, microwave aging repeatability is comparable to that of "RTFOT + PAV".

3. n-Heptane insoluble asphaltenes: It is known that aging causes an increase of the asphaltene content of binder. In the present work, Corbett separation was used to determine asphaltene content of the aged residues obtained after each of the two aging methods. Table 7 shows a good agreement between the asphaltene values obtained for both methods. Except for AAB-1, the difference between the two residues did not exceed 0.8 percent. Asphalt AAB-1 has been reported (15) to have 18.0 percent asphaltene for the "RTFOT + PAV" residue. The 18.0 percent value agrees favorably (1.0 percent difference) with the microwave residue value of 19.0 percent. From Table 7, four asphalts have higher asphaltene content after microwave aging compared with "RTFOT + PAV"; the other four asphalts show the opposite. Thus, aging by either method leads to formation of similar highly polar entities that separate on treatment with an alkane (n-heptane).

4. High-performance size exclusion chromatography (HPSEC): Our previous work (1) has shown that road asphalts subjected to microwave aging give chromatograms that are practically the same as those produced by "RTFOT + PAV" aging. For a given asphalt, the identical chromatograms of the two aged residues are markedly different from that of the neat

material. Therefore, aging either by microwave or "RTFOT + PAV" results in formation of similar molecular associations along the retention time period studied, leading to similar molecular size distributions (1).

5. Relative total polarity: Asphalt total polarity is a fundamental property that apparently controls interactions between a given binder and the field service surroundings: oxygen from the atmosphere, moisture from rain, and aggregate in a mix. Branthaver et al. (12) used ion exchange chromatography to determine experimentally the relative total polarity of four of the core asphalts. The relative total polarity of the core asphalts was found to correlate perfectly (coefficient of determination, $r^2 = 1.00$) with the dielectric heating rate (11). Therefore, it was possible to use the same microwave instrument (used for aging) to determine the dielectric heating rate of each of seven core asphalts, and their aged residues, then calculate the relative total polarity of each, using the curve best-fit equation as described in Ref. 11. Table 8 shows that, as expected, aging by either method causes an increase of the relative total polarity of the neat binders. The table also demonstrates that the two aging methods give essentially the same degree of change in chemical composition, as evident from both the quantity and degree of polarity of the polar constituents; that is, relative total polarity.

6. Infra-red (IR) spectroscopy: One test of aging is to run the IR spectrum that should show formation of the carbonyl function. Researchers usually report the carbonyl region (1800 – 1600 cm^{-1}), and the area under the curve is indicative of the degree of aging (16). The IR spectra of the aged residues obtained by the two aging methods were run at Western Research Institute (WRI). Fig. 1 shows that asphalt AAA-1 undergoes the same level of oxidative aging by "RTFOT + PAV" or microwave energy, as evident from the 1800 – 1600 cm^{-1} region.

Variation of Dynamic Viscosity with Treatment Time

Fig. 2 shows that η^* increases gradually with microwave treatment time. Asphalt AAG-1 has the lowest rate of change, whereas AAD-1 has the highest rate. None of the eight asphalts exhibited the sharp peaks observed previously (17) when pressures of only 130 – 180 psi were used during microwave treatment.

Sample Size

The physical tests associated with the PG system require a rather large amount of material for testing the aged residue. Procedure A of the present work nets about 20 g of aged residue from the 22 g placed in the two vessels used. To increase the process output, six vessels were used per run, each vessel having 11 g of asphalt (procedure B). From a total of 66 g binder, 60 g aged residue can be collected. Tables 9–12 show $G^*.\sin\delta$, S, and m as obtained following procedure B. Comparison between Tables 2 and 10, as well as 5 and 12 show little effect, if any, due to the increase of sample weight. This shows that the microwave energy generated during treatment is enough to age 66 g of binder per run. For Tables 9 and 11, comparing rheological data after "RTFOT + PAV" with those after microwave aging should take into consideration the operator turnover at AI being inevitable over the two year period separating the two sets of measurements.

Microwave (Dielectric) Heating vs. "RTFOT + PAV" (Conductive) Heating

The above data (Tables 1-12, and Fig. 1) show that dielectric heating for 7 hr and 20 min at 143°C and 440 psi yield physical, chemical, and physicochemical changes that parallel those caused by "RTFOT + PAV", that is, conductive heating for 1.5 hr at 163°C, followed by 20 hr at 100°C and 300 psi. To compare, it is noticed that dielectric heating requires a higher temperature and pressure, but shorter time, to achieve the same property changes caused by conductive heating (the PAV conditions of 20 hr at 100°C and 300 psi are the dominant factors contributing to the changes observed after conductive heating). This is not surprising, however, because a number of books (3,4), reviews (6-9), and over 250 papers (6-10, 18-20) report the same observation after investigating numerous types of synthetic organic reactions. That dielectric heating requires a higher temperature (and pressure) to achieve changes comparable to those caused by conductive heating may be due to the inherent heating mechanism involved. Microwave energy causes heating by the rapid rotation (4.9×10^9 times per sec., or twice the frequency of microwaves) of polar molecules, or dipoles, as they align themselves with the applied electromagnetic field (3). A dipole has a number of equilibrium positions that are separated by potential barriers over which the dipole must pass in rotating from one direction to another (6). Therefore, effective dielectric heating occurs at temperatures higher than those associated with conductive heating where no potential barriers nor dipole rotations are involved.

Dielectric and conductive heating: are they interchangeable? A relevant question is whether conductive heating can cause changes similar to dielectric heating, and over the same short time period, if the temperature and pressure of treatment were increased to match those of dielectric heating? That is, can the PAV alone (or after RTFOT), operated at conditions equal to those of microwave aging, lead to similar rheological characteristics? If, under the same conditions, dielectric heating and conductive heating produce the same changes, then the heating mechanism is irrelevant – under those conditions. Table 13 shows that conductive heating may cause some undesirable changes, especially if RTFOT is included. Conductive heating causes AAB-1 to separate into two phases and clumps in the PAV pan. Reheating and stirring restores homogeneity, but integrity of the residue is compromised. The disparity between the two modes of aging is more pronounced for AAD-1 where nonhomogeneity of residue was significant, with and without RTFOT, to the extent that testing was impossible. Note that a pressure of 300 psi was used instead of the 440 psi associated with dielectric heating, because of safety concerns regarding operation of the PAV at such a high pressure (Table 13).

The chemical composition also confirms the physical properties. Fig. 3 compares the IR spectra of the two aged residues of AAB-1. Under the same conditions, it is obvious conductive heating (the upper IR spectrum) causes more severe aging than dielectric heating as evident from the carbonyl region (1800 – 1600 cm^{-1}). IR Spectra for AAD-1 could not be run because of nonhomogeneity of residue after conductive heating. Therefore, raising the PAV temperature, from 100°C, to match the microwave temperature of 143°C does not yield a residue similar to that of microwave aging. At 143°C, the two types of heating are not interchangeable.

Alternatively, the two modes of heating were tested at 100°C (for 20 hr at 300 psi). Table 14 shows that, under these conditions, the effect of dielectric heating is equivalent to conductive heating by "RTFOT + PAV". That is, at 100°C, 20 hr of microwave treatment is equivalent to both 1.5 hr of RTFOT plus the 20 hr of PAV treatment. Tables 13 and 14 prove that the distinct advantage of dielectric heating is observed at temperatures higher than 100°C, e.g., 143°C. At 143°C, only the dielectric heating can simulate the Superpave "RTFOT + PAV", and at a much shorter time (7 hr and 20 min).

CONCLUSION

1. Microwave energy can simulate Superpave "RTFOT + PAV" aging with a 70 percent saving of time. Starting with neat asphalt, microwave treatment for

7 hr and 20 min at 143°C and 440 psi gives a residue equivalent to that of "RTFOT + PAV". This is true for the eight core asphalts – as evident from measurements using six different techniques.

2. Microwave treatment (dielectric heating) at the Superpave conditions of 100°C for 20 hr and 300 psi is equivalent to both RTFOT plus 20 hr PAV (conductive heating) at the same Superpave conditions – as evident from $G^*.\sin\delta$ measurements.
3. An attempt to substitute conductive heating for dielectric heating by raising the PAV temperature to 143°C (to match microwave heating) did not work. After 7 hr and 20 min at 300 psi (440 psi could not be used for safety), the aged residue clumped in the PAV pan, and was so nonhomogenous that rheological testing was not possible. Running RTFOT prior to the PAV (143°C for 7 hr and 20 min, and 300 psi) increased clumping and nonhomogeneity of residue. Furthermore, the carbonyl region of IR spectra indicates distinct excessive aging after "RTFOT + PAV" (7 hr and 20, 143°C, 300 psi) when compared with Superpave "RTFOT + PAV" (20 hr, 100°C, 300 psi).

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Table 1. Intermediate – Temperature Rheological Measurements for the Eight Core Asphalts

Asphalt	Test Temp., °C	"RTFOT + PAV" 20 hr @ 100°C; 300 psi⊕			Microwave Aging 7 hr and 20 min @ 143°C; 440 psi					
					Testing @ KDOT ⊕⊕⊕			Testing @ AI		
		η*, K Poises⊕⊕	G*.sinδ, kPa	Grade	η* K Poises	G*sinδ kPa	Grade	η* K Poises	G*sinδ kPa	Grade
AAA-1	16 13	4,609 7,442	3,480 5,335	16	5,977; 5,263 9,241; 8,012	4,151; 3,759 6,093; 5,449	16; 16	5,458 8,326	3,871 5,642	16
AAB-1	19 16	6,001 9,275	4,191 5,987	19	4,540; 3,947 7,338; 6,462	3,367; 2,981 5,117; 4,610	19; ---; 16	4,411 7,168	3,315 5,106	19
AAC-1	19 16	4,832 7,912	3,687 5,672	19	5,138; 5,460 8,450; 8,993	3,674; 3,912 5,599; 5,978	19; 19	6,044 9,280	4,275 6,199	19
AAD-1	19 16 13	4,467 7,336 ---	3,328 5,150 ---	19	4,365; 3,946 6,831; 6,212 10,270; 9,486	3,163; 2,909 4,737; 4,383 6,805; 6,389	16; 16	3,971 5,786 8,360	2,886 3,954 5,320	16
AAF-1	28 25	4,916 7,483	3,756 5,392	28	5,034; 5,062 8,162; 8,145	3,871; 3,886 5,847; 5,835	28; 28	4,958 7,670	3,727 5,425	28
AAG-1	28 25	4,048 7,432	3,692 6,481	28	4,236; 3,641 7,620; 6,597	3,847; 3,352 6,609; 5,826	28; 28	3,841 6,893	3,511 6,041	28
AAK-1	22 19	6,129 9,505	4,542 6,686	22	4,751; 5,406 7,535; 8,527	3,566; 4,008 5,393; 6,020	22; 22	5,115 7,920	3,767 5,592	22
AAM-1	22 19 16	5,373 8,045 12,106	3,475 4,964 6,840	19	4,169; 4,062 6,649; 6,523 10,669; 10,717	2,903; 2,867 4,328; 4,304 6,411; 6,499	19; 19	4,018 6,336 9,692	2,787 4,130 5,919	19

⊕ All aging and testing at AI.
⊕⊕ η* in K Poises = G* in kPa (ω = 10 rad/s)
⊕⊕⊕ Two separate samples aged and tested at KDOT; the two then mixed and sent to AI for testing.

η* microwave < η* "RTFOT + PAV" for 5 asphalts.
η* microwave > η* "RTFOT + PAV" for 3 asphalts.

Table 2. Critical Intermediate Temperature for the Eight Core Asphalts

Asphalt	Test Temp., °C	"RTFOT + PAV" 20 hr @ 100°C; 300 psi⊕			Microwave Aging 7 hr and 20 min @ 143°C; 440 psi, Testing @ AI			ΔT, °C
		η^*, K Poises⊕⊕	$G^*.\sin\delta$, KPa	T_C, °C	η^* K Poises	$G^*\sin\delta$ kPa	T_C, °C	
AAA-1	16 13	4,609 7,442	3,480 5,335	13.5	5,458 8,326	3,871 5,642	14.0	+0.5
AAB-1	19 16	6,001 9,275	4,191 5,987	17.5	4,411 7,168	3,315 5,106	16.1	-1.4
AAC-1	19 16	4,832 7,912	3,687 5,672	16.9	6,044 9,280	4,275 6,199	17.7	+0.8
AAD-1	19 16 13	4,467 7,336 ---	3,328 5,150 ---	16.2	3,971 5,786 8,360	2,886 3,954 5,320	13.6	-2.6
AAF-1	28 25	4,916 7,483	3,756 5,392	25.6	4,958 7,670	3,727 5,425	25.7	+0.1
AAG-1	28 25	4,048 7,432	3,692 6,481	26.4	3,841 6,893	3,511 6,041	26.0	-0.4
AAK-1	22 19	6,129 9,505	4,542 6,686	21.3	5,115 7,920	3,767 5,592	19.8	-1.5
AAM-1	22 19 16	5,373 8,045 12,106	3,475 4,964 6,840	18.9	4,018 6,336 9,692	2,787 4,130 5,919	17.4	-1.5

$\Delta T_{ave} = 1.2$ °C

⊕ All aging and testing at AI.
⊕⊕ η^* in K Poises = G^* in kPa ($\omega = 10$ rad/s)
⊕⊕⊕ Two separate samples aged and tested at KDOT; the two then mixed and sent to AI for testing.

η^* microwave < η^* "RTFOT + PAV" for 5 asphalts.
η^* microwave > η^* "RTFOT + PAV" for 3 asphalts.

Table 3. Repeatability of Microwave Aging of Asphalt AAD-1 at Intermediate Temperature

Asphalt Sample	G*.sinδ, kPa @ 16°C (KDOT)	G*.sinδ, kPa @ 16°C (AI)
D469	3,760	4,368
D470	4,058	4,462
D471	4,751	4,321
D472	4,909	4,450
D474	4,350	4,322
D475	3,903	4,165
	KDOT Data Spread = 4909 – 3760 = 1149 $\overline{\chi} = 4335$ % Variation = $\frac{1149 \times 100}{4335} = 26.5\%$	AI Data Spread = 4462 – 4165 = 297 $\overline{\chi} = 4314$ % Variation = $\frac{297 \times 100}{4314} = 6.9\%$

Acceptable range for 6 results = 7.9 x 4.0 = 31.6%
For TP5: C.V. single operator (1s%) = 7.9
From ASTM C670: for 6 samples, multiply C.V. x 4.0

Table 4. Low-Temperature Rheological Measurements for the Eight Core Asphalts

Asphalt	Temp., °C	"RTFOT + PAV" 20 hr @ 100°C; 300 psi			Microwave 7 hr and 20 min @ 143°C; 440 psi		
		S, MPa	m	grade	S, MPa	m	grade
AAA-1	-18 -24	149 367	0.376 0.318	-28	140 317	0.352 0.299	-28
AAB-1	-18 -24	280 505	0.307 0.246	-28	196 448	0.327 0.267	-28
AAC-1	-12 -18 -24	137 296 547	0.343 0.280 0.234	-22	127 281 533	0.347 0.289 0.232	-22
AAD-1	-18 -24	207 397	0.349 0.291	-28	167 365	0.352 0.292	-28
AAF-1	-6 -12	124 291	0.369 0.292	-16	128 267	0.353 0.289	-16
AAG-1	-6 -12	244 528	0.392 0.280	-16	213 506	0.405 0.290	-16
AAK-1	-12 -18 -24	154 329 627	0.391 0.309 0.246	-22	139; 114 ----; 270 ----; 508	0.372; 0.392 ---- ; 0.321 ---- ; 0.250	-28
AAM-1	-12 -18	179 367	0.306 0.265	-22	167 325	0.309 0.255	-22

All testing at AI.

Table 5. Critical Low Temperature for the Eight Core Asphalts

Asphalt	Temp., °C	"RTFOT + PAV" 20 hr @ 100°C; 300 psi			Microwave 7 hr and 20 min @ 143°C; 440 psi			ΔT_C, °C
		S, MPa	m	T_C, °C	S, MPa	m	T_C, °C	
AAA-1	-18 -24	149 367	0.376 0.318	-32.2	140 317	0.352 0.299	-33.4	-1.2
AAB-1	-18 -24	280 505	0.307 0.246	-28.5	196 448	0.327 0.267	-30.5	-2.0
AAC-1	-12 -18 -24	137 296 547	0.343 0.280 0.234	-26.1	127 281 533	0.347 0.289 0.232	-26.9	-0.8
AAD-1	-18 -24	207 397	0.349 0.291	-30.9	167 365	0.352 0.292	-32.0	-1.1
AAF-1	-6 -12	124 291	0.369 0.292	-20.7	128 267	0.353 0.289	-21.0	+0.3
AAG-1	-6 -12	244 528	0.392 0.280	-17.2	213 506	0.405 0.290	-17.8	-0.6
AAK-1	-12 -18 -24	154 329 627	0.391 0.309 0.246	-27.4	139; 114 ----; 270 ----; 508	0.372; 0.392 ---- ; 0.321 ---- ; 0.250	-28.8	-1.4
AAM-1	-12 -18	179 367	0.306 0.265	-22.9	167 325	0.309 0.255	-23.0	-0.1

$\Delta T_{ave} = 0.9°C$

All testing at AI.

Table 6. Repeatability of Microwave Aging for Asphalt AAD-1 at Low Temperature

Asphalt Sample	S, MPa* @ -18°C	m* @ -18°C
D469	155	0.366
D470	151	0.366
D471	160	0.356
D472	167	0.343
D474	156	0.360
D475	155	0.362
	For S Spread = 167 – 151 = 16 $\overline{\chi} = 159$ % Variation = $\frac{16 \times 100}{159} = 10.1\%$	For m Spread = 0.366 – 0.343 = 0.023 $\overline{\chi} = 0.355$ % Variation = $\frac{0.023 \times 100}{0.355} = 6.5\%$

* At AI

Acceptable range for 6 results for S = 3.2 x 4.0 = 12.8%
Acceptable range for 6 results for m = 1.4 x 4.0 = 5.6%
For TP1: C.V. Single operator (1s%) for S = 3.2; for m = 1.4
From ASTM C670: for 6 samples, multiply C.V. x 4.0

Table 7. Comparison Between Asphaltene Content Obtained after the Two Aging Methods

Asphalt	n-Heptane Asphaltene, % (Corbett)	
	"RTFOT + PAV"	Microwave Energy
AAA-1	22.9	23.7
AAB-1	20.8*	19.0
AAC-1	15.1	15.2
AAD-1	28.5	28.0
AAF-1	18.2	18.6
AAG-1	9.2	9.0
AAK-1	26.4	26.0
AAM-1	7.5	7.7

* Ref. 15 reports 18.0% for heptane asphaltenes after "RTFOT + PAV" aging.

Table 8. Effect of Aging Method on Asphalt Relative Total Polarity

Asphalt	Neat	"RTFOT + PAV"* (20 Hr @ 100°C, 300 psi)	Microwave* (7hr and 20 min @ 143°C,440 psi)
AAA-1	111.0	114.5	113.9
AAB-1	107.1	111.3	109.4
AAC-1	102.9	106.2	106.4
AAF-1	104.0	108.3	107.0
AAG-1	105.4	107.5	107.4
AAK-1	112.5	115.8	114.7
AAM-1	96.8	103.8	102.7

* Calculated as described in Ref. 11.

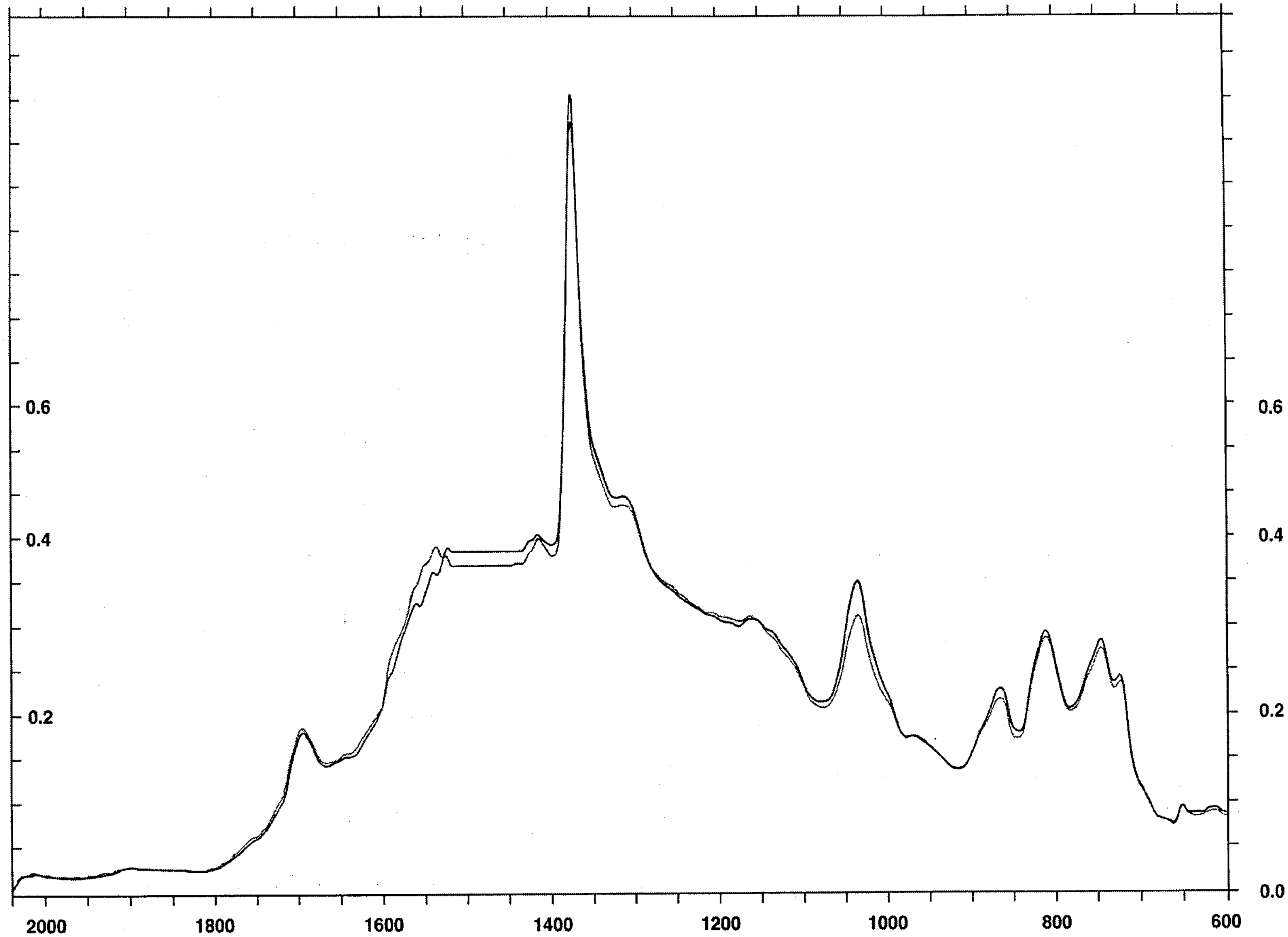

Fig. 1. IR Spectra asphalt AAA-1 after aging by "RTFOt + PAV" vs. microwave energy.

Fig. 2. Effect of Microwave Treatment Time on η* for the 8 Core Asphalts

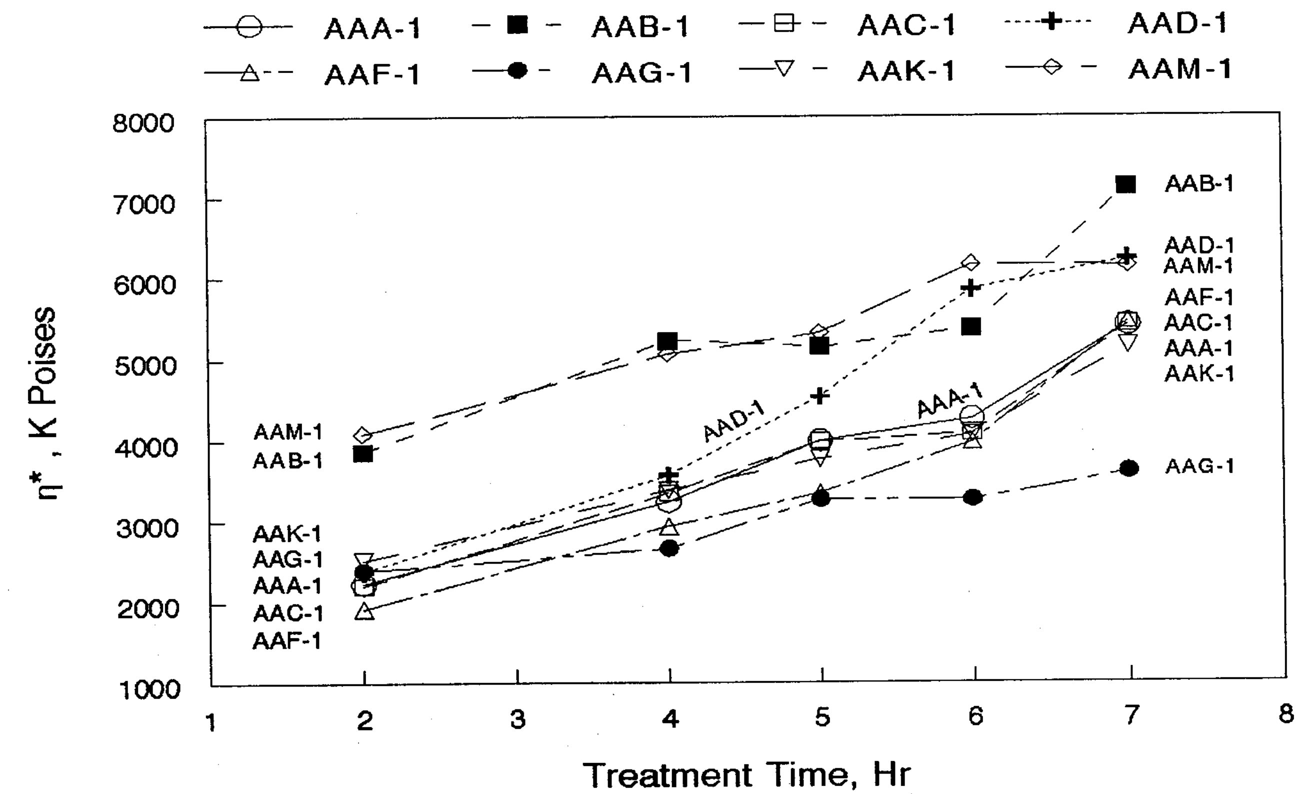

Table 9. Intermediate – Temperature Rheological Measurements after aging (6 x 11)g binder

Asphalt	Test Temp., °C	"RTFOT + PAV" 20 hr @ 100°C; 300 psi⊕			Microwave Aging 7 hr and 20 min @ 143°C; 440 psi					
					Testing @ AI			Testing @ KDOT		
		η*, K Poises⊕⊕	G*.sinδ, K Pa	Grade	η* K Poises	G*sinδ K Pa	Grade	η* K Poises	G*sinδ K Pa	Grade
AAA-1	16	4,609	3,480	16	5,209	3,653	16	4,900	3,421	16
	13	7,442	5,335		7,893	5,298		7,539	5,011	
AAB-1	19	6,001	4,191	19	3,457	2,644		3,644	2,782	
	16	9,275	5,987		5,686	4,125	16	5,806	4,210	16
	13	----	----		8,768	6,028		9,223	6,281	
AAC-1	19	4,832	3,687	19	3,668	2,809		4,447	3,365	19
	16	7,912	5,672		6,212	4,461	16	7,317	5,196	
AAD-1	19	4,467	3,328	19	3,949	2,831		3,573	2,574	
	16	7,336	5,150		6,085	4,203	16	5,540	3,829	16
	13	---	---		9,212	6,100		8,422	5,562	
AAF-1	28	4,916	3,756	28	4,298	3,346	28	4,474	3,407	28
	25	7,483	5,392		6,991	5,112		7,168	5,095	
AAG-1	28	4,048	3,692	28	3,448	3,180	28	3,572	3,292	28
	25	7,432	6,481		6,397	5,661		6,509	5,734	
AAK-1	22	6,129	4,542	22	2,994	2,389		3,385	2,688	
	19	9,505	6,686		4,875	3,743	19	5,505	4,190	19
	16	----	----		7,750	5,702		8,739	6,341	
AAM-1	22	5,373	3,475		2,864	2,131		3,207	2,357	
	19	8,045	4,964	19	4,574	3,198		5,185	3,583	19
	16	12,106	6,840		7,192	4,690	16	8,201	5,272	

⊕ All aging and testing @ AI.

⊕⊕ η* in K Poises = G* in K Pa (ω = 10 rad/s)

Table 10. Critical Intermediate Temperature after aging (6 x 11)g binder

Asphalt	Test Temp., °C	"RTFOT + PAV" 20 hr @ 100°C; 300 psi⊕			Microwave Aging 7 hr and 20 min @ 143°C; 440 psi Testing @ AI			ΔT, °C
		η*, K Poises⊕⊕	G*.sinδ, K Pa	T_C, °C	η* K Poises	G*sinδ K Pa	T_C, °C	
AAA-1	16 13	4,609 7,442	3,480 5,335	13.5	5,209 7,893	3,653 5,298	13.5	-0.0
AAB-1	19 16 13	6,001 9,275 ----	4,191 5,987 ----	17.5	3,457 5,686 8,768	2,644 4,125 6,028	14.5	-3.0
AAC-1	19 16	4,832 7,912	3,687 5,672	16.9	3,668 6,212	2,809 4,461	15.3	-1.6
AAD-1	19 16 13	4,467 7,336 ---	3,328 5,150 ---	16.2	3,949 6,085 9,212	2,831 4,203 6,100	14.6	-1.6
AAF-1	28 25	4,916 7,483	3,756 5,392	25.6	4,298 6,991	3,346 5,112	25.2	-0.4
AAG-1	28 25	4,048 7,432	3,692 6,481	26.4	3,448 6,397	3,180 5,661	25.6	-0.8
AAK-1	22 19 16	6,129 9,505 ----	4,542 6,686 ----	21.3	2,994 4,875 7,750	2,389 3,743 5,702	16.9	-4.4
AAM-1	22 19 16	5,373 8,045 12,106	3,475 4,964 6,840	18.9	2,864 4,574 7,192	2,131 3,198 4,690	15.5	-3.4

$\Delta T_{ave} = 2.1°C$

⊕ All aging and testing @ AI.

⊕⊕ η* in K Poises = G* in K Pa (ω = 10 rad/s)

Table 11. Low-Temp Rheological Measurements after aging (6 x 11)g binder

Asphalt	Temp., °C	"RTFOT + PAV" 20 hr @ 100°C; 300 psi			Microwave 7 hr and 20 min @ 143°C; 440 psi		
		S, MPa	m	grade	S, MPa	m	grade
AAA-1	-18	149	0.376	-28	135	0.347	-28
	-24	367	0.318		293	0.297	
AAB-1	-18	280	0.307	-28	196	0.319	-28
	-24	505	0.246		407	0.264	
AAC-1	-12	137	0.343	-22	107	0.369	-28
	-18	296	0.280		248	0.301	
	-24	547	0.234		450	0.251	
AAD-1	-18	207	0.349	-28	152	0.343	-28
	-24	397	0.291		333	0.304	
AAF-1	-6	124	0.369	-16	116	0.357	-16
	-12	291	0.292		232	0.291	
	-18	----	----		447	0.226	
AAG-1	-6	244	0.392	-16	183	0.399	-16
	-12	528	0.280		436	0.290	
AAK-1	-12	154	0.391	-22	91	0.411	-28
	-18	329	0.309		249	0.332	
	-24	627	0.246		512	0.265	
AAM-1	-12	179	0.306	-22	150	0.331	-22
	-18	367	0.265		326	0.267	

"RTFOT + PAV" aging and all low-temperature testing was conducted at AI.

Table 12. Critical Low Temp after aging (6 x 11)g binder

Asphalt	Temp., °C	"RTFOT + PAV" 20 hr @ 100°C; 300 psi			Microwave 7 hr and 20 min @ 143°C; 440 psi			ΔT_C, °C
		S, MPa	m	T_C, °C	S, MPa	m	T_C, °C	
AAA-1	-18	149	0.376	-32.2	135	0.347	-33.6	-1.4
	-24	367	0.318		293	0.297		
AAB-1	-18	280	0.307	-28.5	196	0.319	-30.1	-1.6
	-24	505	0.246		407	0.264		
AAC-1	-12	137	0.343	-26.1	107	0.369	-28.1	-2.0
	-18	296	0.280		248	0.301		
	-24	547	0.234		450	0.251		
AAD-1	-18	207	0.349	-30.9	152	0.343	-32.9	-2.0
	-24	397	0.291		333	0.304		
AAF-1	-6	124	0.369	-20.7	116	0.357	-21.2	-0.5
	-12	291	0.292		232	0.291		
	-18	----	----		447	0.226		
AAG-1	-6	244	0.392	-17.2	183	0.399	-18.8	-1.6
	-12	528	0.280		436	0.290		
AAK-1	-12	154	0.391	-27.4	91	0.411	-29.2	-1.8
	-18	329	0.309		249	0.332		
	-24	627	0.246		512	0.265		
AAM-1	-12	179	0.306	-22.9	150	0.331	-24.9	-2.0
	-18	367	0.265		326	0.267		

$\Delta T_{ave} = 1.6°C$

"RTFOT + PAV" aging and all low-temperature testing was conducted at AI.

Table 13. Rheological Properties after Dielectric Heating vs. Conductive Heating Under the Same Conditions

Asphalt	Property	Test Temp, °C	Microwave or Dielectric Heating (**7 hr and 20 min**; 143°C; 300psi)	PAV or Conductive Heating (**7 hr and 20 min**; 143°C; 300 psi)		Observation
				No RTFOT	RTFOT + PAV	
AAB-1	G", kPa	22°C 19°C 16°C 13°C	1657 2616 4075 ----	3704 5691	4054 5536	"AAB-1 showed signs of separation and clumping after PAV aging, but was homogenous after reheating and stirring." AI
	S, MPa	-12°C -18°C -24°C	---- 181 410	131 258 ----	139 275 ----	
	m	-12°C -18°C -24°C	---- 0.339 0.276	0.313 0.269 ----	0.304 0.265 ----	
AAD-1	G", kPa	19°C 16°C 13°C 10°C	---- 3254 4991 7509	---- ---- ---- ----	---- ---- ---- ----	"AAD-1 with and without RTFOT were non-homogenous after PAV aging, and therefore could not be tested." AI
	S, MPa	-18°C -24°C	139 324	---- ----	---- ----	
	m	-18°C -24°C	0.387 0.317	---- ----	---- ----	

All measurements at Asphalt Institute (AI).

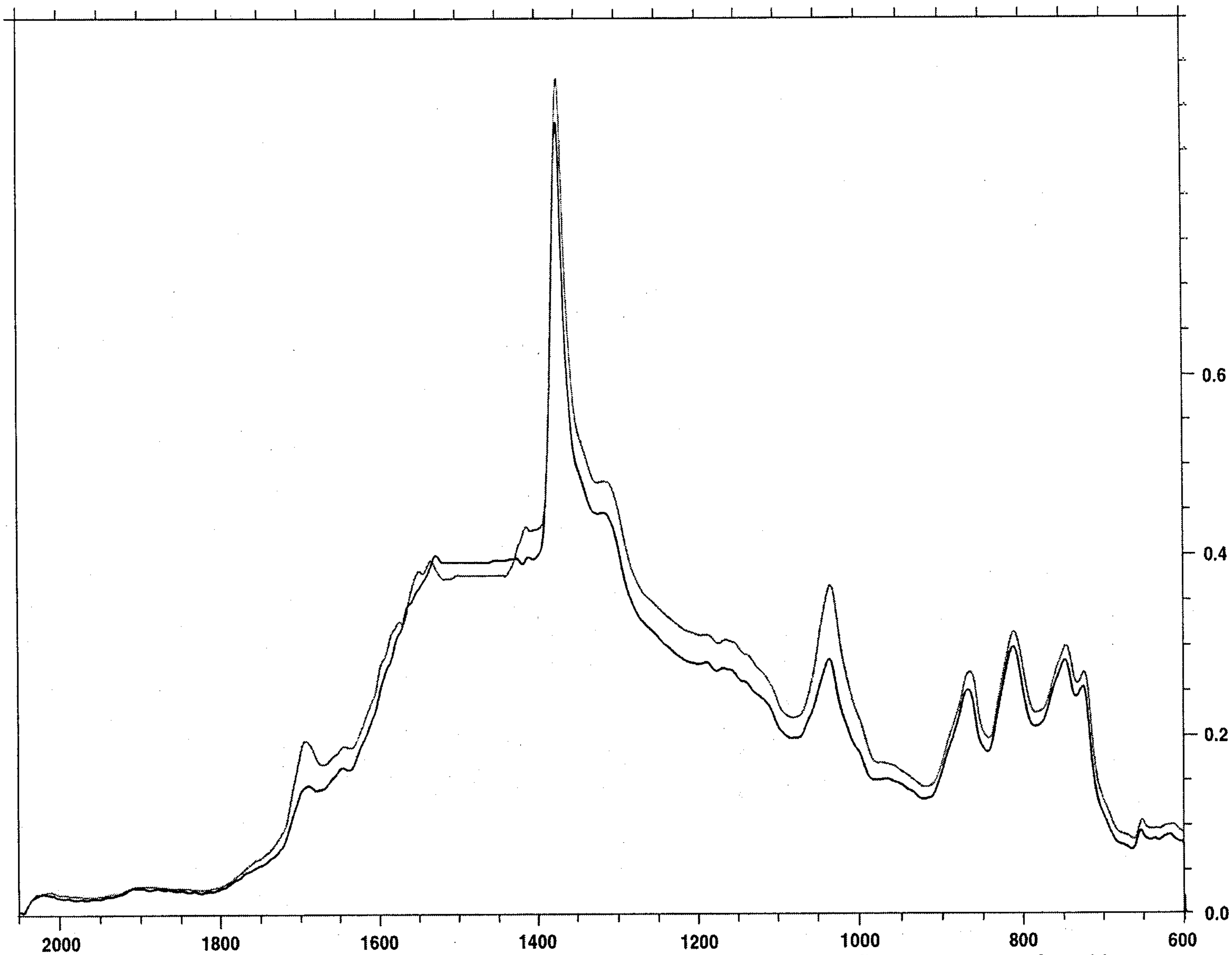

Fig. 3. IR spectra of two residues of AAB-1 after aging by microwave energy (lower spectrum) and by "RTFOT + PAV", under the same conditions.

Table 14. Intermediate – Temperature Stiffness after Dielectric and Conductive heating – both Run at Superpave Conditions

Asphalt	Test Temp., °C	"RTFOT + PAV" 20 Hr; 100°C; 300 psi (Conductive)	Microwave 20 Hr; 100°C; 300 psi (Dielectric)
AAF-1	28	3,756	3,061
	25	5,392	4,747
AAC-1	19	3,687	3,392
	16	5,672	5,295